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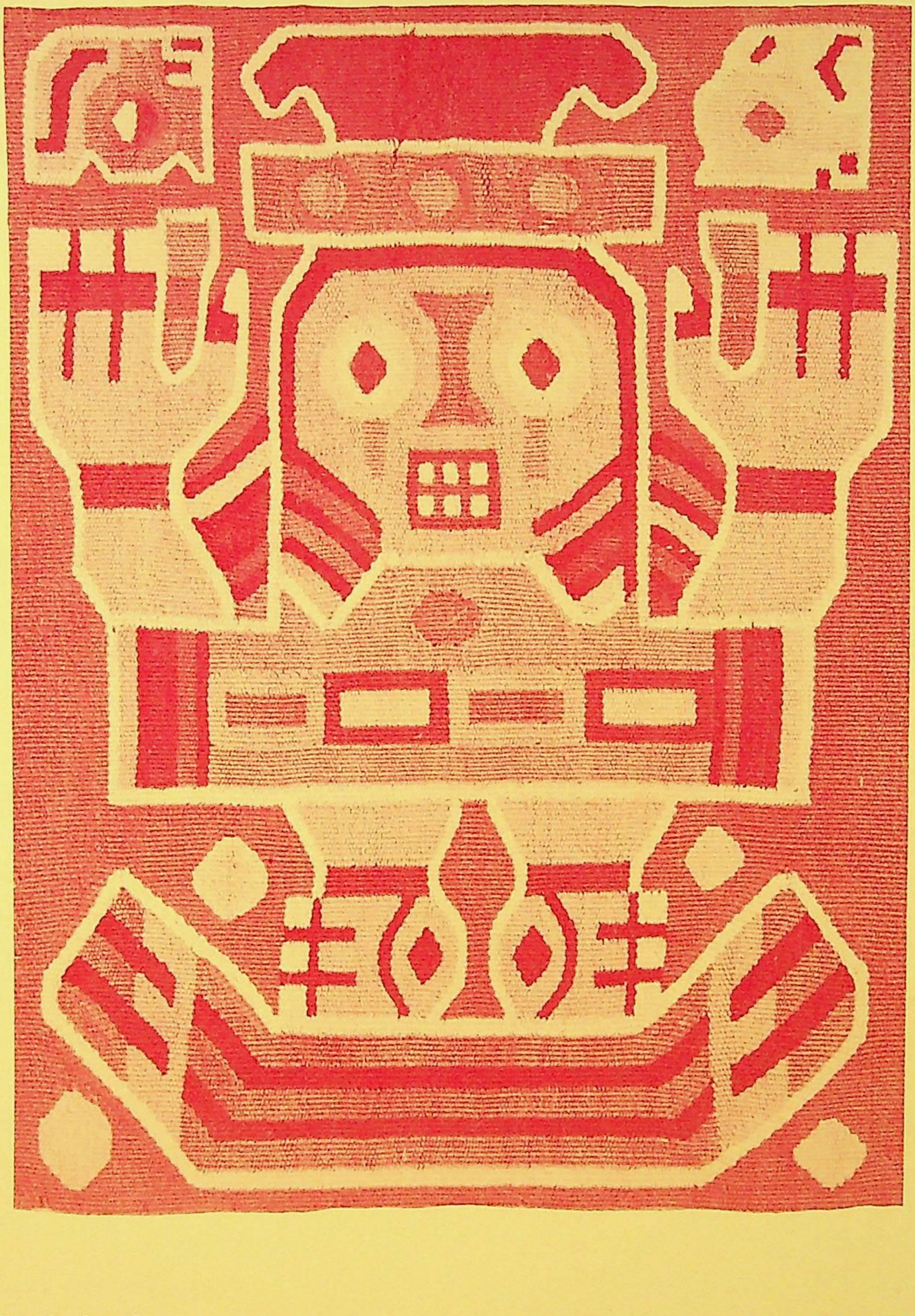

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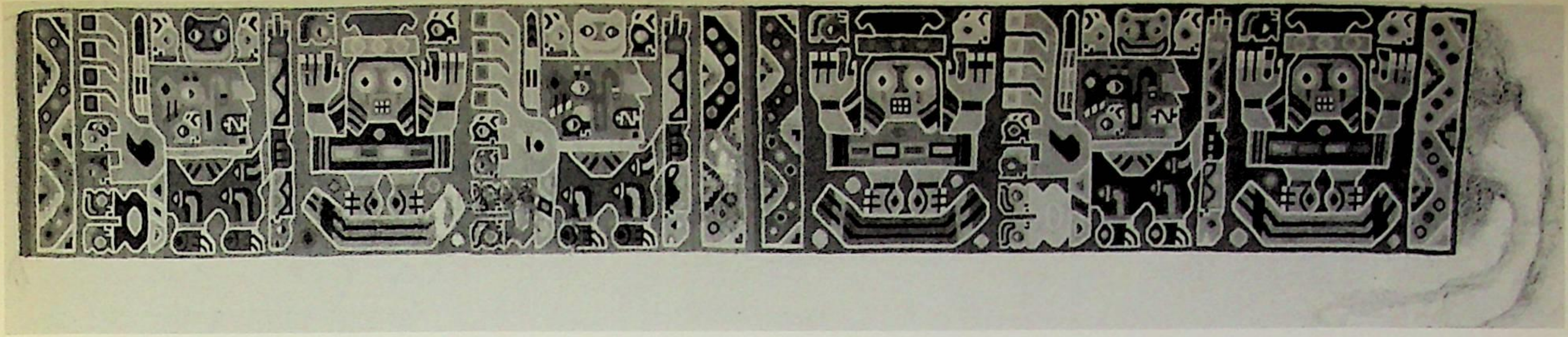

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DRAWINGS by Milton Franklin Sonday, Jr.

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PRINCIPLES OF TEXTILE CONSERVATION SCIENCE NO. VI

THE WONDERS OF WATER IN WETCLEANING

James W. Rice

Although cleaning has been necessary ever since protective and decorative garments and other textiles were first devised, it has only been in the last half century that its complex scientific nature has been understood. The servicing of fabrics in this connection seems to have lagged behind their invention and development and it is our impression that museum textile conservation has not taken advantage of all of the most modern techniques and scientific advances. For this reason, we have composed this article to relate our museum type textile problems to the latest professional cleaning practices.

What Should We Do Before Starting A Textile Cleaning Job?

In analyzing the problems of cleaning, we believe that successful solutions therefor will require an attack in a sequence of five steps which are listed in Figure 1 and discussed in greater detail later.

Figure 1 *ANALYSIS OF CLEANING PROBLEMS*

1. Physical Condition
2. Soils and Colorants
3. Cleaning Media
4. Cleaning Methods
5. Cleaning Aids

First: An accurate knowledge of the physical condition and constitution of the specimen under study is essential.

Second: Closely related to its condition are the soils and products of decomposition and ageing which may mask its beauty and lessen its value. The types and characteristics of the dyes and colorants should be established at this time also.

Third: A decision as to the cleaning medium to be chosen is required at this time, based on the results of the studies made in the first two steps. The cleaning media referred to here are air, water, and organic liquids, Figure 2. The peculiarities of air and water will be discussed in this paper. The organic liquids will be the subject of later papers in this series.

Fourth: Based on information obtained in the examination and testing steps and the decision as to cleansing medium, it becomes necessary at this point to make a second decision as to the mechanical treatment and methods of cleaning. This is founded on the studies of the physical condition and strength made in the inspection steps.

Fifth: At this stage, it becomes necessary to establish the additives and cleaning aids that will enable us to do the job with the least changes to the textile specimen. At this time, decisions are made as to detergents, dye setting or bleeding agents, bleaches if required, temperatures and timing of the operations within the cleaning medium and how the excess medium is to be removed, together with the various aspects of drying and prevention of dimensional change.

Principles concerning how to choose detergents and similar cleaning aids will be discussed in another paper shortly. Other matters just mentioned will be presented later in forthcoming articles.

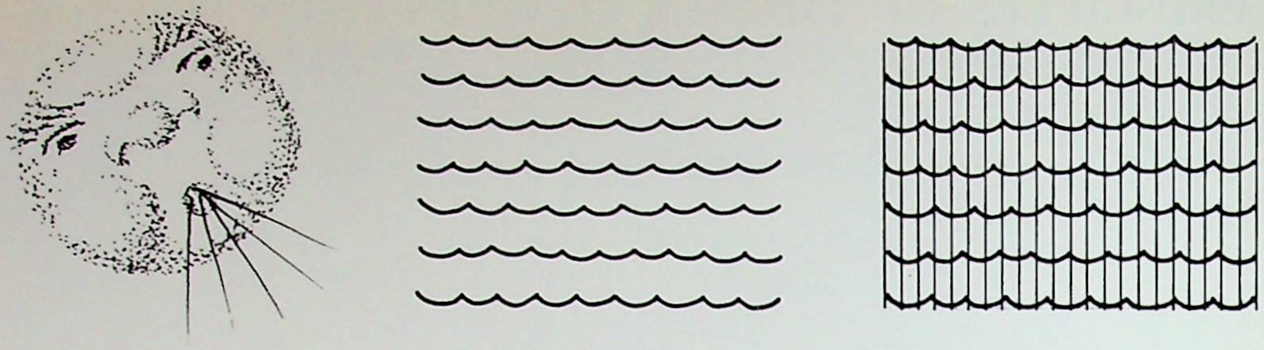
What are the Cleaning Media?

Of the three main types of cleaning agents mentioned, air is relatively unimportant. It is suitable for removal of comparatively large, nonadhered dirt particles, lint, fiber fragments and other light foreign trash. Its effectiveness depends on the lifting and carrying powers of an air blast and can be modified by humidity and mechanical agitation of the fabric. It is readily available, cheap, and, because the mechanical action can be controlled easily, perhaps the least likely to cause physical damage to the specimen. Cleaning is actually limited and the results may not be satisfactory. Its cleaning effectiveness can be increased by adding abrasives and absorbent powders as, for example, in sand blasting of metals or sawdust in cleaning furs.

This paper is particularly concerned with wetcleaning or the wonderful ways that water works in washing.

Why is Water Such A Good Cleaning Medium?

Water is the best known and most widely used of the three fluid cleaning systems, but it is probable that many of us never stop to think about the unique chemical and physical properties that make it such a good cleaning agent. Also we may not know why it fails under the conditions in which



AIR WATER ORGANIC SOLVENTS

Figure 2

it comes to us. The purpose of this article is to describe how, by the help of additives, temperature controls, mechanical manipulations and special treatments, its effectiveness can be increased and its deficiencies overcome.

Water has been called the universal solvent and for this reason is the most useful cleaning fluid. Because it is such a good solvent, it is likely to be contaminated with dissolved substances and undesirable suspended matter. However, if filtered and free of bacteria or fungae, and chemicals such as strong acids, strong alkalies, iron salts and chlorides, it will probably be suitable and safe for most textile cleaning.

What Happens When Water Dissolves Most Inorganic Substances?

Water is a remarkable liquid because not only will it dissolve organic substances such as sugars, starches, gelatins, colored stains and dyes, it also has the peculiar power of causing many inorganic chemicals to split up into electrically charged particles. These are called ions and are either negative or positive. The process is called ionization.

When ionized, chemical compounds are able to exchange ions freely, which on collision form new substances. If these happen to be insoluble in water or if soluble and do not re-ionize after joining, the products may be removed from the action scene. Water is one of the very few chemicals that has ionization powers. In many instances, success in cleaning depends on our management of the behavior of a number of the different ions so a brief presentation of ways of controlling them is made at this time.

Can Water Itself Be Ionized?

Water is a simple chemical compound, being composed of two atoms of hydrogen combined with one atom of oxygen, empirically represented by the formula H_2O. Structurally, we write it as HOH. The reason for this last abbreviation is that unless a great deal of energy is expended, water does not break down into the elements hydrogen and oxygen but will itself ionize to a very limited extent into hydrogen ions (H^+) and hydroxyl ions (^-OH), Figure 3. Thus the chemical formula HOH is most representative of these two special ions, both of which have a very great influence on cleaning. As a rule, the hydrogen ion retards soil and stain removal, whereas the hydroxyl ion favors cleaning.

$$H_2O$$

$$HOH \longrightarrow H^+ + {}^-OH$$

Figure 3

What Is An Acid? An Alkali?

Absolutely pure water contains only one free hydrogen ion and one free hydroxyl ion in ten million molecules of the liquid. At this point it is neutral. Substances that will increase the concentration of hydrogen ions when dissolved in water are acids. Other substances that increase the concentration of hydroxyl ions are called bases or alkalies, the latter being defined as water soluble bases.

What Is Neutralization?

Acids and alkalies are opposing classes of chemical compounds and when their solutions are brought together, will form water and a salt, Figure 4. When the resulting solution is balanced at the neutral point of water mentioned above, we say that the solution has been neutralized.

What Is the pH System of Describing Acidity or Alkalinity?

In a widely used numerical comparison system of describing the degree of acidity, called pH, the neutral point is given the value of pH 7. In this system pH 0 is most acid and pH 14 is least acid or most alkaline.

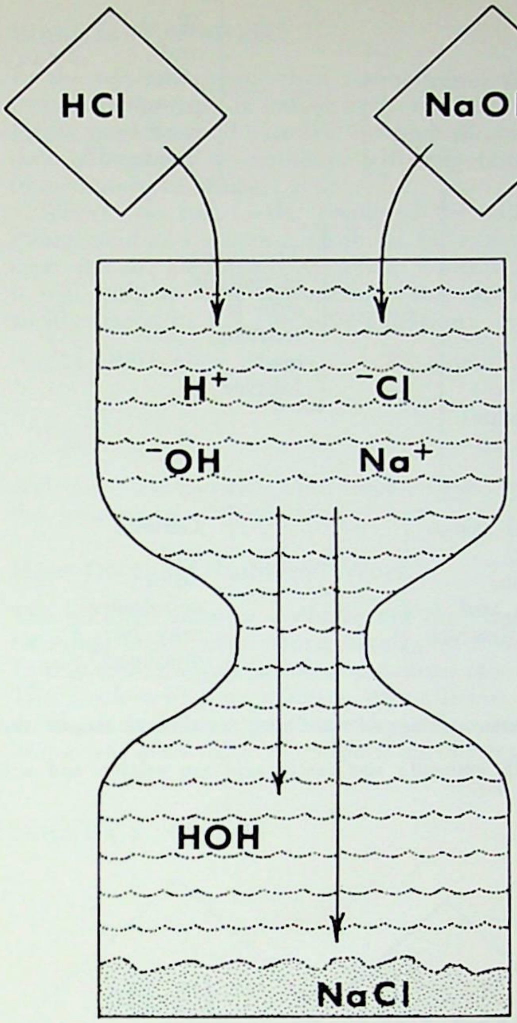


Figure 4

A pH chart indicating the more important properties of water at various degrees of acidity, as far as textile cleaning is concerned, is shown by the accompanying illustration, Figure 5. Note that the safety zone for textile cleaning ranges from an acidity of about pH 4 to an alkalinity of about pH 10. Except for unusual soil or stain conditions, we should maintain our cleaning solutions within these limits.

Why Are Wash Water Solutions Made Alkaline?

Because most soils and natural stains are acidic, washing solutions as counteractants must usually be alkaline. Thus alkalies in some form are added. This is also necessary, because soft water is often acidic and cleaning is much better under alkaline conditions. At this point control of the pH becomes necessary and how pH may be regulated becomes important.

Obviously a very few drops of an acid or alkali would produce a minimum change. A larger quantity would increase or decrease the pH, as the case may be. This is not satisfactory, because of difficulties in determining the precise amounts to be added.

What Are Strong Acids? Why Avoid Them?

Fortunately, not all substances ionize to the same extent when dissolved in water. In the case of the acids, three—hydrochloric, sulfuric and nitric—will ionize completely. These are called strong acids because a very small amount will produce a pH approaching the maximum acidity point of zero (0). Most of the other acids, which we will call weak, will ionize only partially. The extent of ionization of the weak acids will vary with the particular compound, and its concentration in the solution. An example of this is acetic acid, the sour principle of vinegar, which at 0.1% produces a pH of about 3 and does not change appreciably when the concentration is increased tenfold. The acetic acid dissolves completely but only a small part ionizes, leaving a reservoir of unionized but readily available acid in the solution, Figure 6.

What Are Strong Alkalies? Why Avoid Them?

There are a few strong alkalies, namely sodium hydroxide and potassium hydroxide, which ionize completely and approach pH 14 when a little is dissolved in water. The remainder are weak. A classic example of which is ammonium hydroxide (aqua ammonia) which at 0.1% concentration produces a pH of about 9, but does not change greatly on adding more, Figure 7. Both acetic acid and ammonium hydroxide are popular cleaning reagents because they are volatile and, on evaporating, do not concentrate on the fabric. Consequently, the pH or ^-OH or H^+ ion-effects cannot become damaging on drying the material.

How May Excessive Alkalinity or Acidity Be Controlled?

Where it becomes necessary to provide permanent acidity or alkalinity at a specified pH in a textile, or an even more closely controlled pH condition in a solution, we may resort to the use of "buffering" type chemicals, known to the industry as "soap builders" and "Laundry sours." The builders are alkali forming salts, while the sours are acid forming salts.

What Is a Salt?

In order to explain how these chemicals work, it will be necessary for us to recall that when acids and alkalies are mixed in solution in the proper proportions, neutralization results and a "salt" and water are formed. By evaporating the water, we can separate the salt in its crystaline or solid form.

from the water to remain free. This unbalances the neutrality in favor of alkalinity and the pH registers above the neutral point pH 7. As these hydroxyl ions are used up, more can be furnished by the water and the pH level will remain constant. Figure 9.

How Do the "Sours" Work?

The acids producing salts are formed by a combination of a weak alkali and a strong acid, such as hydrochloric, sulfuric or nitric acids. In the same fashion as just explained, the weak metallic ion of an acid forming salt captures a hydroxyl ion from the water and thus frees a hydrogen ion. The number of these is limited, but the pH is unbalanced below the neutral point of pH 7. When used, their replacement follows the same pattern as explained above. Figure 10.

Without the hydrolysis theory mechanism, we would have great difficulty in controlling soil removal and dye losses in cleaning.

Three rules that may be helpful aids in selecting acid forming and alkali forming salts:

1. Strong acids and strong alkalies form neutral salts.
2. A salt of a strong acid and a weak alkali is acidic.
3. A salt of a strong alkali and a weak acid is alkaline.

What Is "Hard" Water?

Before the advent and widespread availability of modern synthetic detergents, soft water was a necessity for good textile washing results. Where the water was "hard," a great deal of trouble was taken to soften it.

Hard water may be defined as water that contains dissolved salts of metals, principally calcium, magnesium and iron. These hardness forming chemicals are picked up by the water as it flows through the ground and combine chemically with true soaps to form insoluble sticky soap curds which have no cleaning properties and deposit out on the work to produce an undesirable graying of the fabric.

What Is the Principle of Surface Ion Exchange Water Softening?

Formerly, many recipes for cleaning called for rain water or distilled water, both of which are condensed from water vapor and, in doing so, leave the objectionable non-volatile hardness salts behind. Because rain water is usually not dependable nor plentiful in many temperate regions and distillation is an expensive process, many users of large quantities of soft water now employ surface ion exchange principles for water softening. In this case, the hard water is passed through a bed of granules of zeolite, a natural mineral, or one of the more recently developed synthetic resin granules with increased surface ion acceptance and exchange abilities. Figure 11.

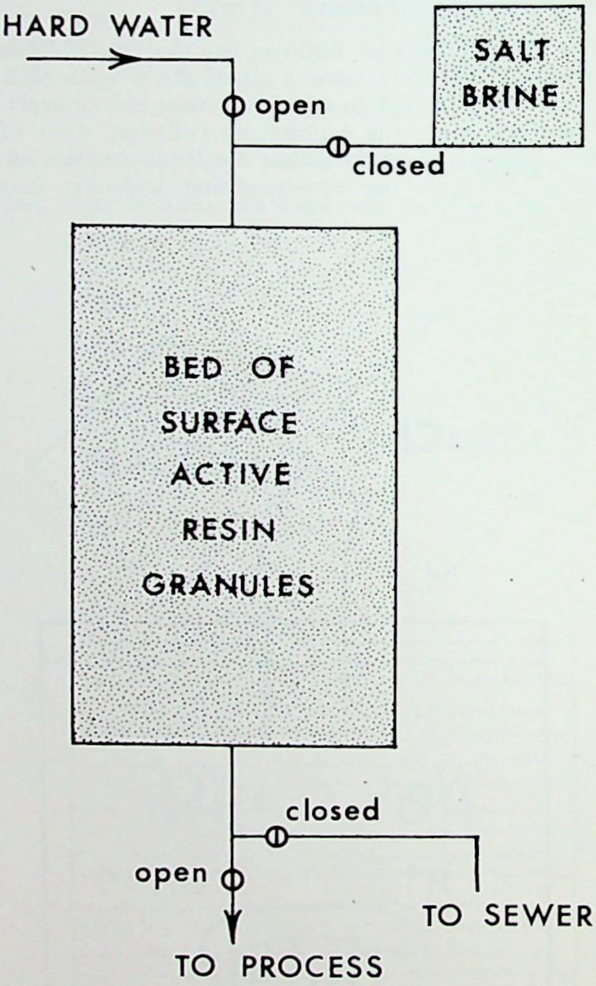


Figure 11

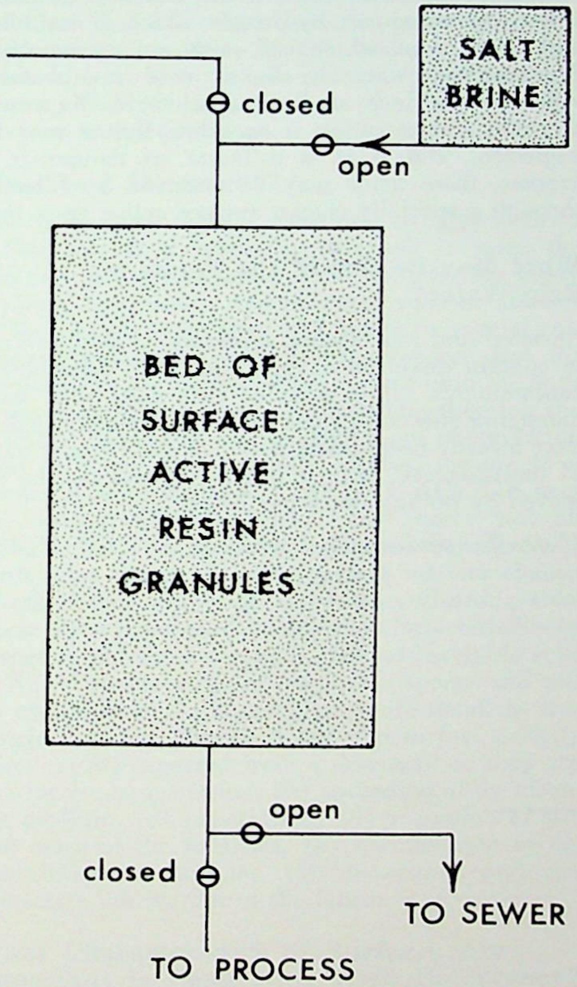


Figure 12

The zeolites or resins are complex insoluble chemicals which have the peculiar power of adsorbing certain ions, as for example sodium, onto their surfaces. They also have an attraction for other ions such as calcium, magnesium, ferrous iron and others, providing the concentration of these hardness substances in the water is greater than that of any of the sodium ions present in the solution. In this case, an exchange takes place and the hardness ions deposit on the resin, releasing sodium ions which are non-hardness forming because they make soluble soaps and not the soap curds.

If water, containing a high concentration of sodium ions such as in strong salt brine, is passed through the zeolite bed, the exchange is reversed and the mineral or resin can be rejuvenated. The effluent in this case contains the hardness ions and is run to the sewer for disposal. Figure 12.

The development of synthetic resins for ion exchange has brought about treatments that can produce contamination free water which is not possible in distillation even with very great care.

The cost of equipment and operations for ion exchange systems is much less than the cost of distillation, and will be satisfactory for almost all washing purposes.

What Is the Principle of Complex Ion Formation?

Complex ion formation by sequestrants or chelating agents is another popular modern way of removing undesirable ions from washing waters. The sequestrating agents are chemical compounds that are already composed of a complex ion which has a peculiar power of exchanging non-hardness forming ions from within the ionic structure for one of the common hardness producing ions. A case in point is the action of sodium hexametaphosphate on soluble calcium salts, as illustrated by the chemical equation and Figures 13 and 14:

$$2CaSO_4 + Na_2\ (Na_4\ (PO_3)_6) \rightarrow$$

water hardness	complex ion

$$Na_2SO_4 + Na_2\ (Ca_2\ (PO_3)_6)$$

soft water	complex ion containing soluble calcium

This same chemical sequestrant is also capable of exchanging sodium ions for calcium in precipitated soap curds and is one way to brighten textiles grayed in previous cleanings.

In other instances, the chelating agent reacts directly with the unwanted ion to form a complex molecule which may or may not be soluble but which does not permit it to react with any other ion. Modern physiological chemistry is full of illustrations to support this. One of the most spectacular being the control of ferric iron poisoning by desferrioxamine B, a long chain molecule that is sup-

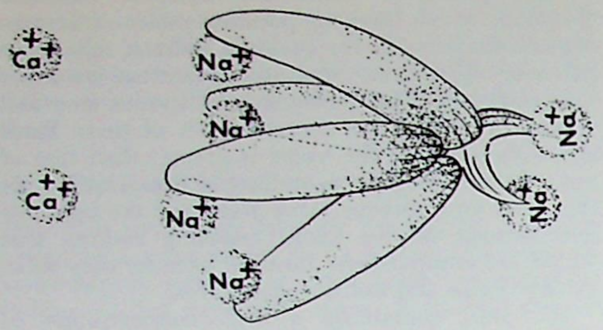


Figure 13

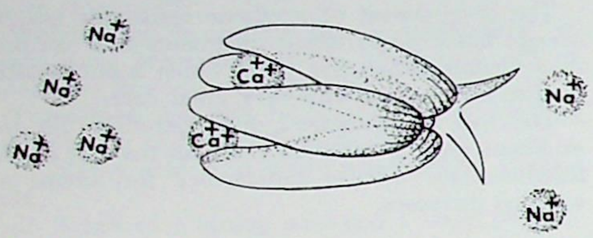


Figure 14

posed to entwine itself around the ferric atom and prevent it from reacting. In the reduced state as ferrous ions, the sequestration may be accomplished by citric acid, oxalic acid, hydroflouric acid or Calgon*, but some of these might not be tolerated within the living body, as such, and thus might be toxic themselves.

What Other Troublesome Ions Are Sometimes Encountered?

Other ions that might be considered as unwelcome in water for washing purposes are chlorides, nitrates, sulfides and, on occasion, copper or other more rare metals from saline lakes, wells, springs, and industrial wastes. Any of these may be removed by distillation, chelation or by surface active resin treatments. In each case, the nuisance must be diagnosed and the most effective treatment prescribed.

How Do We Usually Get Rid of Suspended Matter, (Muddy Water)?

Suspended matter is ordinarily cleared by coagulation with a flocculation agent such as an aluminum salt, either alum or aluminum chloride. This causes emulsified micelles in suspension to coagulate into particle sizes that can be removed by sand filters. Any free aluminum ions, if the water is aerated, will form aluminum hydroxide which is insoluble and forms a gel which will settle out on standing. The resulting water is slightly acid and contains either hydrochloric acid or sulfuric acid. As a rule, the acid concentration is so dilute that it may be neglected. But if it is a factor of danger in a process, these acids may be removed by filtering through a specially chosen surface active resin bed.

What May Be One of the Faults of Rain Water?

Aerated and rain waters, especially if cold, are apt to contain dissolved oxygen and other atmospheric contaminants. It is possible that these may have damaging effects on some textiles, especially if they have already been oxidized in ageing. Usually most of the dissolved oxygen and acid gases can be removed by boiling the water before use.

(**signifies trade-marked product*)

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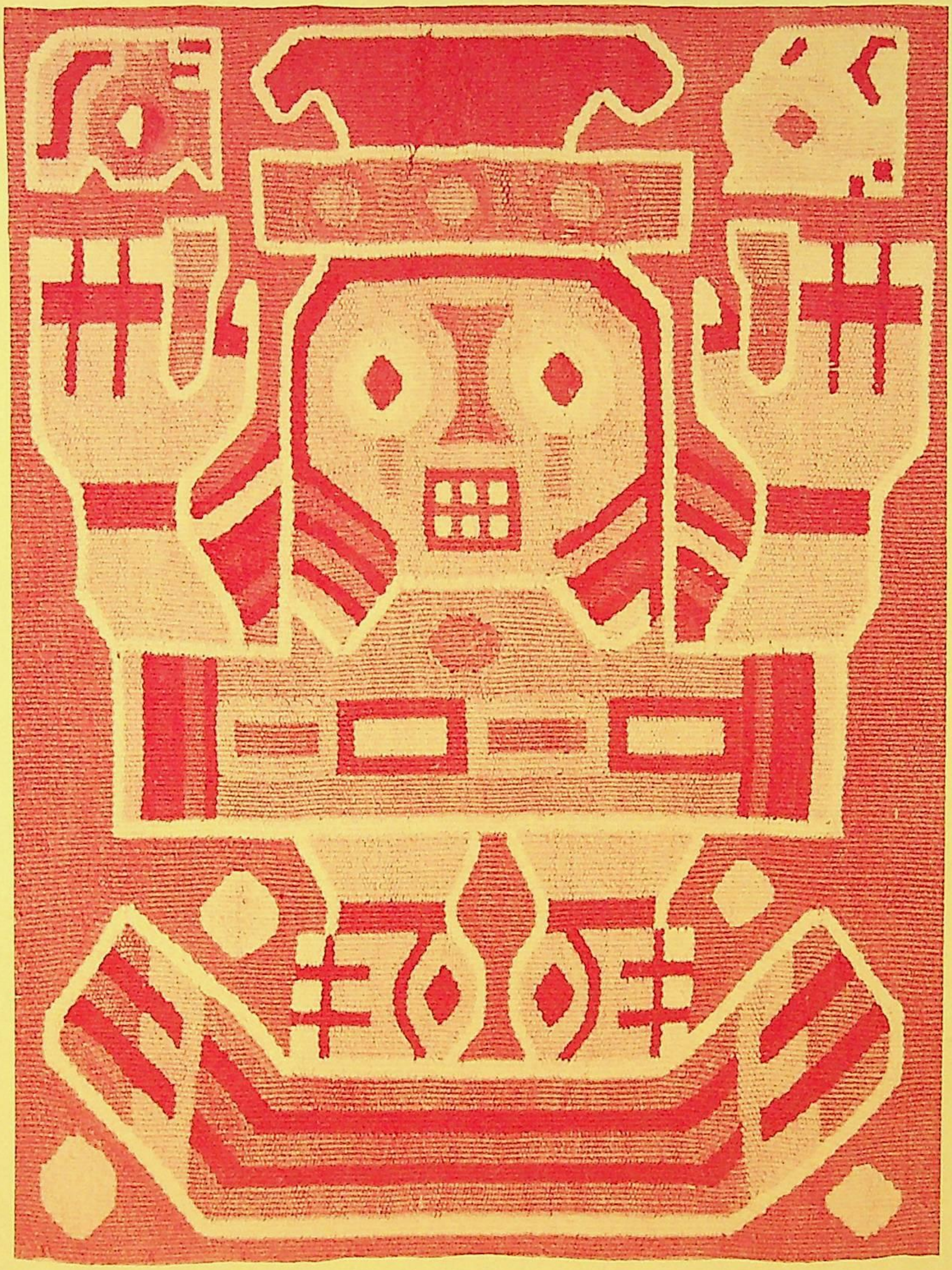

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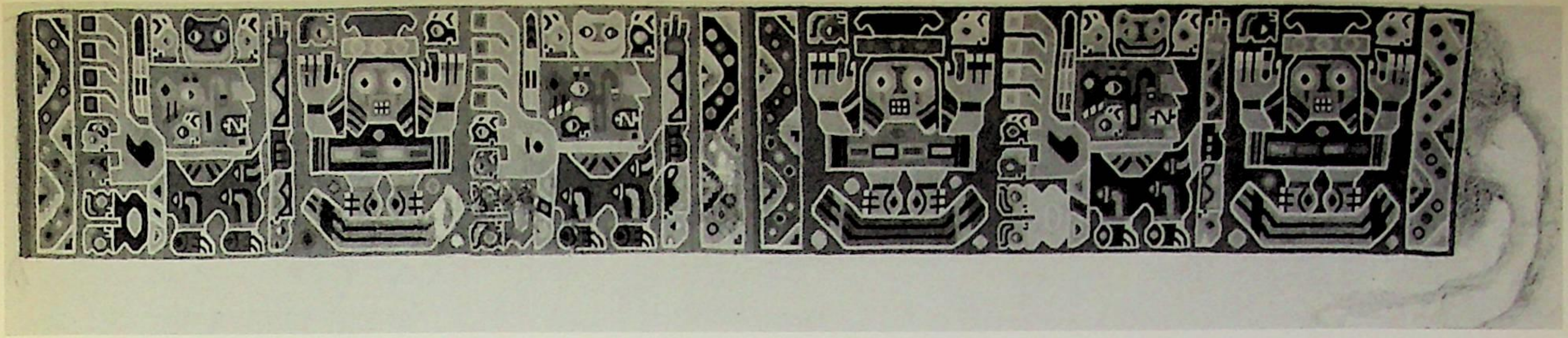

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